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EFFECTS OF ZINC POWDER ADDITION TO VILLA GLOSS AND SILKA LUX MARINE ENAMEL PAINTS ON CORROSION RESISTANCE OF MILD STEEL

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Abstract: The most common method of protecting steels and other similar engineering materials from corrosion is by painting or coating. Development in the paint industries suggests that the modern paints exhibit improved corrosion resistance over their predecessors. However, anti-corrosion properties of the paints can further be optimized when adequate proportions of the paint constituents are used. Effect of zinc powder addition to Villa Gloss and Silka Lux Marine Enamel paints on corrosion resistance of mild steel was studied. The results indicate that zinc powder addition between 15 and 25 % significantly reduced the corrosion rate and thus increased the inhibition efficiency of mild steel immersed in seawater. The corrosion rate stabilizes at approximately 0.10 mmpy when zinc powder added was above 15 %, independent of the exposure time. Potentiodynamic anodic polarization curves of the samples immersed in seawater show that sample with 25 % zinc powder addition exhibited highest corrosion potential and the least corrosion current. Microstructural analysis of the samples also revealed the presence of pit corrosion at the surfaces of the samples and their geometry, volume fraction and distribution vary with the zinc powder addition.

Keywords: Zinc powder, inhibition efficiency, potentiodynamic anodic polarization, seawater, corrosion rate

INTRODUCTION

Painting or coatings of all kinds are often used to provide interior and exterior decoration, which makes the environment appealing. Painting is a major method of protecting metal surfaces from different types of corrosion and its application is comparatively easy with no limitation on the size of the steelwork or materials that can be treated. Hence, painting of all kinds is very attractive and convenient means of corrosion control. Besides decoration and corrosion prevention purposes, painting or coating of surfaces can also serve purposes such as light reflectivity, camouflaging surfaces and heat absorber [1], [2].

Paintings of steelwork and other surfaces are very useful. However, deterioration and degradation of paints set-in over time and thus corrosion of surfaces is inevitable. Commonest among the causes of earlier corrosion are deficient surface preparation [3], insufficient coating thickness [4], [5], incorrect formulation of paint by the manufacturer [6], [7], inadequate skill of the painter, wrong choice of paints, drastically change in environmental conditions, mechanical or human physical damage.

Incorrect formulation of paint by manufacturer seems to be a major challenge in corrosion prevention [7]. This is because all other causes of corrosion can be corrected prior to paint application but wrong formulation required new production. The principal ingredients of paints are pigments, fillers, co-reactant and surfactant [1]. Each of these ingredients is required in a certain proportion for the formulation and performance properties. The atoms of the ingredients join together to form molecules, which crosslinks with one another, the reactive sites of each of the reacting molecules must align and come within very close proximity to each other for coating. Basically, the main function of the metallic

pigments is to form sacrificial metallic oxides with the environment or seawater [8]. However, paints with inadequate metallic pigments corrode earlier and the steel underneath is exposed for chemical attack. For example, when a scratch or a break occurs in a zinc-rich paint film, water and oxygen combine with the metallic zinc. Over time, the zinc particles will corrode away and the paint's protective ability will be lost.

Investigations have been conducted to examine the effect of metallic pigments on corrosion control of steels immersed in corrosive media. In the study of Fayomi and Popoola, the electrochemical behaviour and the corrosion properties of Zn coating on steel substrates by means of Vickers micro hardness and polarization measurements was investigated [9]. Effect of graphite addition on the corrosion resistance and mechanical properties of zinc chromate epoxy paint was evaluated by Mirhabibi et al. [10]. They declared that addition of graphite decreases the corrosion rate and impact resistance while the resistance against the abrasion increases due to hydrophobic properties of the graphite. In a similar study by Durodola et al. In their work, steel substrate was coated with zinc and immersed in seawater and compared with uncoated steel. They concluded that coated steel performed better than uncoated steel substrate [11]. Abdou and Yaser studied the effect of recent three types coatings used in marine ship surfaces for prevention against corrosion. They revealed that coating significantly enhance the corrosion protection of coated sample by 70 % when compared to the uncoated sample [8]. In this current study, the effect of zinc powder addition on corrosion properties of Villa Gloss and Silka Lux Marine Enamel paints was examined. The objective of this article is to investigate the benefit that zinc powder addition as on the paints for corrosion control.

MATERIALS AND METHODS

Materials

The materials used for this study are mild steel, paints (red and white colours), zinc powder, seawater, distilled water, emery papers, ethanol, digital weighing balance, hack saw, laboratory beaker, flask and plastic brush.

The mild steel used in this work was obtained from Niger Dock Nigeria PLC, Lagos, Nigeria. The red and white paints were procured from local vendors in Lagos State, Nigeria. The nominal chemical composition of mild steel and paints are given in Table 1 and Table 2 respectively.

Table 1: Chemical Composition of the Mild Steel used (Wt %)

C	Si	Mn	P	S
0.129	0.242	1.35	0.0148	0.0031
Cr	Mo	Ni	Al	Co
0.0187	0.0011	0.0015	0.027	0.0040
Cu	Nb	Ti	V	W
0.008	0.004	0.001	0.0057	0.007
Pb	Sn	Mg	As	Zr
0.002	0.0035	0.001	0.003	0.0015
Bi	Ca	Ce	Sb	Se
0.002	0.001	0.0015	0.0025	0.0037
Te	Ta	B	Zn	Fe
0.0027	0.0430	0.0014	0.003	98.1

Table 2: Atomic Absorption Spectrophotometric Results of Analysed Red and White Paints

Paint types	Zinc (mg/L)	Calcium (mg/L)
Villa Gloss (white paint)	0.2817	2.009
Silka Lux Marine Enamel (red paint)	1.6618	24.57
Blank	0.001	0.001

Table 3: The Nominal Chemical Composition of the Zinc Powder

Elements (%)	Cd	Ca	Fe	Cu	Sn	Zn
	0.200	4.200	0.010	0.005	0.010	95.570

Table 3 is the chemical composition of zinc powder used. The chemical composition of the corrosive medium (seawater) used is also presented in Table 4. Metal analyzer was used to obtain the chemical composition of the mild steel and zinc powder while atomic absorption spectrophotometer shown in Figure 1 (a) was used for the paints.

Preparation of samples and its immersion procedure

The as-received mild steel was machined into test samples of dimensions of 2.20 cm by 1.50 cm by 1.16 cm. The samples were smoothed on emery papers of 80, 150 and 320 grits. The samples were washed in distilled water with a plastic brush and then soaked in an ethanol for 5 minutes. Subsequently, the samples were allowed to sun dried for 10 minutes.

The test samples were individually designated for easy identification (see Nomenclature). The test samples were then coated sacrificially with two different commercial paints that have varying percentages by weight of zinc powder addition (see Nomenclature) and Figure 1c. The coating thickness ranged between 10 and 20 μm , which classify the coating process adopted as thin films [14]. The initial weight (W_i) of the sample was taken using a digital weighing scale.

Table 4: Chemical Composition of Seawater

Parameters	Unit	Results	Maximum Permitted [12], [13]	Health Effect
Seawater				
pH	-	6.47	6.5-8.5	None
Conductivity	$\mu\text{S}/\text{cm}^3$	4940.00	1000	None
Total hardness	mg/L	150.00	150	None
Total alkalinity	mg/L	50.00	50	-
Total acidity	mg/L	50.00	50	-
Calcium	mg/L	60.12	50	-
Magnesium	mg/L	21.84	0.20	Consumer Acceptability
Chloride	mg/L	15083.98	250	None
Salinity	mg/L	27250.00		
Copper	mg/L	0.072	1	Gastrointestinal disorder
Iron	mg/L	0.69	0.3	None
Zinc	mg/L	0.169	3	None
Lead	mg/L	0.09	0.01	Cancer
Cadmium	mg/L	0.002	0.003	Toxic to kidney
Nickel	mg/L	0.16	0.02	Possibly carcinogenic
Chromium	mg/L	0.051	0.05	Cancer

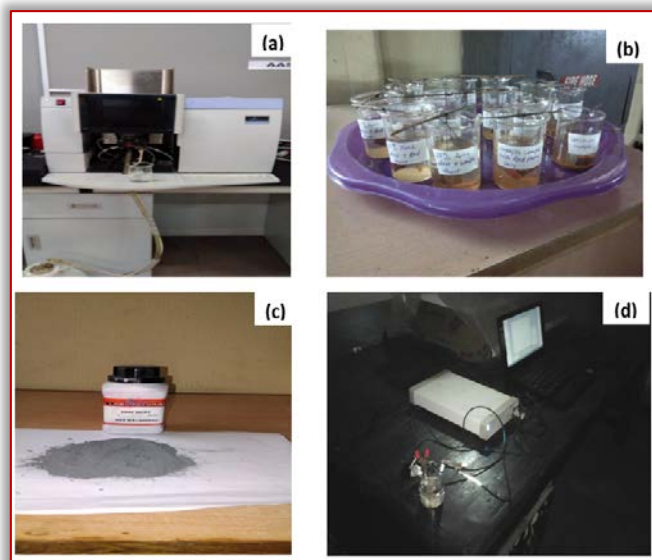


Figure 1: The laboratory set-up and material used a) Atomic Absorption Spectrophotometer, (b) Experimental Set-up, (c) Commercial Zinc Powder and (d) Potentiodynamic polarization test set-up

Thereafter, equal proportion of analyzed corrosive medium was measured out with laboratory beaker and poured in a transparent flasks. The samples were then completely immersed in the corrosive medium (see Figure 1b). After every 3-day (72-hour) of immersion, individual sample was

brought out of the corrosive medium and then gently and thoroughly cleaned with distilled water and ethanol and then weighted for final weight (W_2). The weight loss (W_t) obtained was then used to calculate the corrosion rate. In all cases, the processes of samples cleaning, washing, drying, weighing were thoroughly and gently carried out – since the data collection largely depend on these processes [15].

Quantitative Analysis Method

This work employed a quantitative analysis techniques for the determination of the corrosion rate based on the weight loss method. It involved taken the weight loss (W_t) of uncoated and coated samples before and after immersion in the corrosive medium. The corrosion rate was calculated according to the formulae (1) and (2) [8].

$$\text{Corrosion rate (mmpy)} = \frac{87.6 * \text{weight loss } (W_t)}{\text{Area } (A) * \text{time}(T) * \text{Density}(\rho)} \quad (1)$$

where

$$\text{Surface area } (A) = 2[L * B] + (L * H) + (B * H) \quad (2)$$

The weight loss was also used to calculate the surface coverage and Inhibition Efficiency according to formulae (3) and (4) respectively after 1800 hours.

$$\text{Surface Coverage, SC} = \frac{CR_a - CR_p}{CR_a} \quad (3)$$

$$\text{Inhibition Efficiency, IE (\%)} = 100SC \quad (4)$$

where CR_a and CR_p are corrosion rates in the absence and presence of the inhibitor, respectively.

Potentiodynamic Polarization Technique

Potentiodynamic polarization test was performed with cylindrical steel electrodes mounted in acrylic resin. The steel electrode was prepared according to ASTM G59-97 [16]. The studies were performed at 25°C ambient temperature with Digi-lyv 2300 potentiostat and electrode cell containing 200 ml of the acid media (see Figure 1 d). Platinum was used as the counter electrode and silver chloride electrode (Ag/AgCl) was employed as the reference electrode. Potentiodynamic measurement was performed from -1.5V to +1.5V at a scan rate of 0.0015 V/s according to ASTM G102-89 [16]. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were derived from the Tafel plots of potential versus log current.

Preparation of Samples for Microstructural Analysis

The corroded samples were examined with an optical microscope for surface defects. Prior to the microstructural examination, each of the samples was dried in an oven at 30°C for 5 minutes.

RESULTS AND DISCUSSION

Corrosion Rate and Inhibition Efficiency

In this study, two types of industrial paints were used: Villa Gloss (white paint) and Silka Lux Marine Enamel (red paint). The atomic absorption spectrophotometric analysis of the two paints indicates that the red paint is of higher zinc and calcium constituents than the white paint (see Table 2). The chemical analysis of the corrosive medium used was shown in Table 4. The calcium, salinity and chloride (mm/L) that are present in corrosive medium are well above the required limit

for a normal water [12], [13]. Thus, the sea water used is suitable for this study.

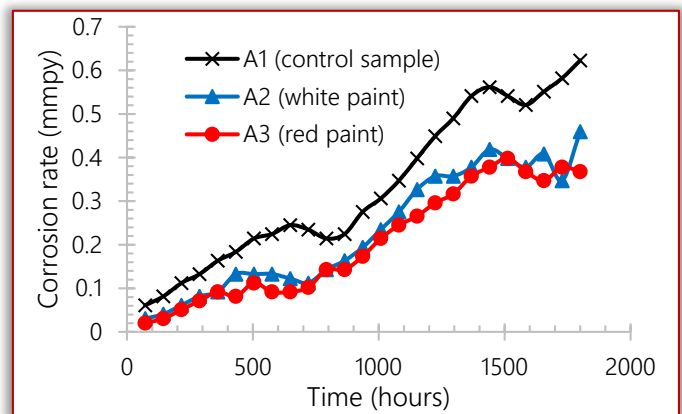


Figure 2: Variation of Corrosion Rate with Exposure Time for Mild Steel without Zn Powder Addition

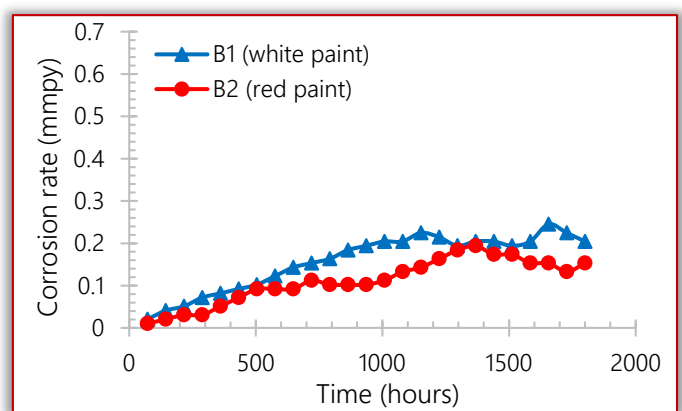


Figure 3: Variation of Corrosion Rate with Exposure Time for Mild Steel with 5 % Zn Powder Addition

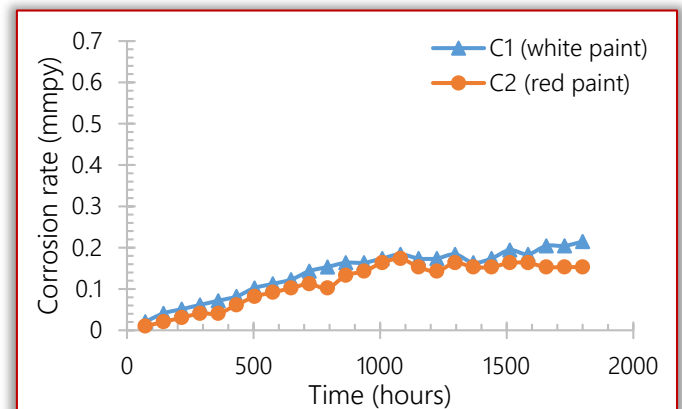


Figure 4: Variation of Corrosion Rate with Exposure Time for Mild Steel with 10 % Zn Powder Addition

Figures 2-4 show the variation of the corrosion rate with the time of exposure for the mild steel coated with varied zinc powder addition. Figure 2 indicates that for the control sample and as-procured paints, corrosion rate increased with exposure time. However, it decreased as the percent of zinc powder addition is increased as shown in Figures 3 and 4. The decreasing in the corrosion rate with 5 to 25 % addition of zinc powder is shown in Figures 5 and 6. In general, coating of the mild steel significantly reduces the corrosion rate as compared to the uncoated sample. The initial slow rate of the

corrosion at exposure time less 700 hours is due to the formation of a barrier between the substrate and the sea water. Thus, the mild steel is isolated from the aggressive corrosion of the seawater due to the passivation of zinc. Above 1100 hours, passivation can also be noticed with stability in the corrosion rate (Figures 3 & 4). In this condition, corrosion products, which provides a protective layer has been formed. It can also be deduced from Figures 3 and 4 that for the same exposure time, the red paint performed credibly well than the white paint, evidence in it lower corrosion rate. The effect of zinc powder addition to the paints on the corrosion rate is less significant when the exposure time exceeded 1500 hours.

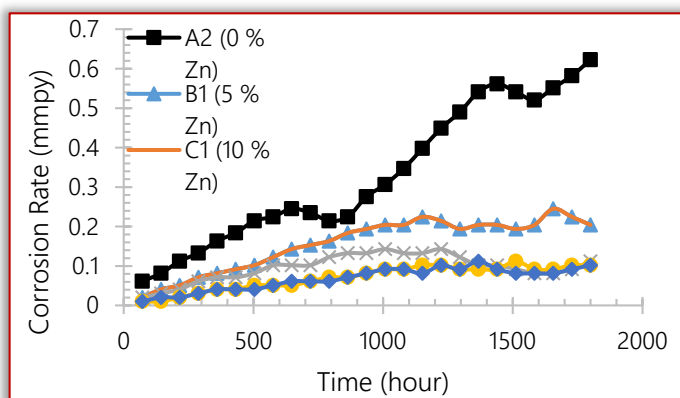


Figure 5: Variation of Corrosion Rate with Exposure Time for Mild Steel Coated in Red with 0-25% Zn Powder Addition

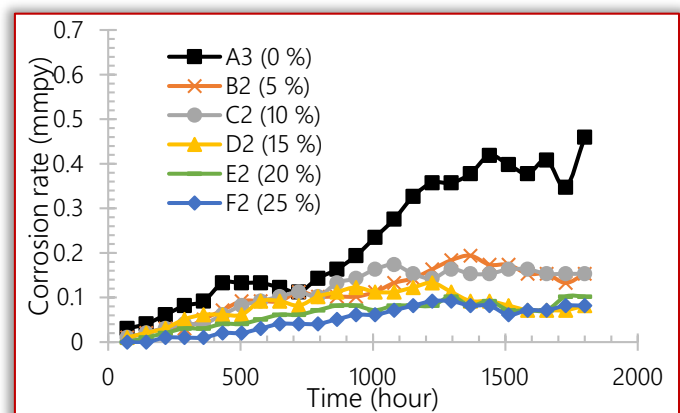


Figure 6: Variation of Corrosion Rate with Exposure Time for Mild Steel Coated in White with 0-25% Zn Powder Addition

The colour change in the corrosive medium over the exposure time play a major role in determining the extent of corrosion rate. In this study, the main constituents of the paints are calcium and zinc elements. The colour of the corrosive medium that contain control sample turned completely dark while the coated samples were observed to be colourless and later lightly dark due to the formation iron oxide of the former and CaCl_2 and ZnCl_2 in the later. Zinc is sacrificial coatings that lessen the corrosion on the mild steel underneath. As it can be noticed in Figures 5 and 6 that the corrosion rate of the samples with 15 to 25 % zinc powder addition stabilises at 0.10 mmpy. At optimum zinc powder addition, corrosion rate stabilises due to the conversion of the zinc to zinc trioxocarbonate IV (ZnCO_3) during the natural

corrosion cycle. The zinc constituent is converted to zinc oxide (ZnO) and later to zinc hydroxide depends on the water and air presence in the sea water. Further reaction of ZnO (white rust) with CO_2 (carbon IV oxide) formed ZnCO_3 , which is corrosion product that is impermeable to the seawater and very dense layer [17]. Thus, with 15 to 25 % zinc powder addition, a barrier is formed that prevent further corrosion of mild steel underneath.

The experimental results indicate that the adhesion of corrosion product of ZnCO_3 layer is effective. The protection demonstrated by the layer, however, depends on the pH of the environment [18]. The corrosion rate changes in an acidic or basic, which ultimately dissolve the ZnCO_3 layer with time. The reaction is more aggressive in acidic medium than basic. In this study, the pH of the seawater used is 6.47, as shown in Table 4. Thus, it is expected that within 15 to 25 % zinc powder addition and seawater under investigation, the effect of pH is minimal and erosion of ZnCO_3 is low or absent.

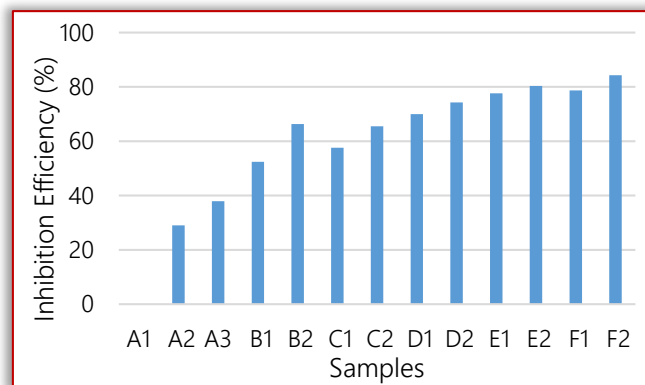


Figure 7: Dependence of Inhibition Efficiency on Sample Processing Condition for Mild Steel Painted in Red and White with 0-25% Zn Powder Addition

Figure 7 shows the dependence of inhibition efficiency on the types of paints and zinc powder addition. The inhibition efficiency was obtained from surface coverage (SC). The inhibition efficiency increases with zinc powder addition. Red paint exhibits higher inhibition efficiency over white paint for the same zinc powder addition due to higher proportion of the zinc present in the as-procured red paint. Above 15 %, the effect of zinc powder addition for the two paints on the inhibition efficiency is less significant. This suggests that there is an optimum zinc and calcium mixing composition that is required in a paint to achieve effective and protective layer, which ultimately reduces and stabilise the corrosion rate. On one hand, zinc and calcium present in the paint formed a barrier between mild steel and the sea water, which increases the inhibition efficiency. On the other hand, the formation of CaCl_2 and ZnCl_2 tends to reduce the inhibition efficiency. However, saturation of the CaCl_2 and ZnCl_2 within the seawater stabilise the inhibition efficiency. Figure 8 is the result of total corrosion rate as function of types of paints and zinc powder addition. Stability in the corrosion rate corresponds to zinc powder 15 to 25 % addition.

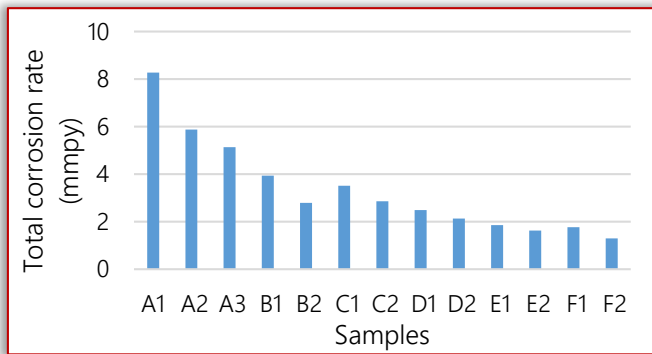


Figure 8: Dependence of Total Corrosion Rate on Sample Processing Condition for Mild Steel Painted in Red and White with 0-25% Zn Powder Addition

□ Potentiodynamic Polarization Technique

Figure 9 shows the potentiodynamic anodic polarization curves of the mild steel immersed in seawater with and without zinc powder addition. The corrosion potential from the figure tends towards the positive direction for all samples except for the control sample. This shows the inhibiting effect of the paints and zinc powder added. The samples with zinc powder addition display active-passive polarization behaviour. Table 5 shows the electrochemical corrosion parameters derived from the potentiodynamic polarisation curves shown in Figure 9. By single out the corrosion potential and corrosion current for the analysis, the addition of zinc powder causes an increase in corrosion potential and a decrease in corrosion density. Apparently, the ratio of calcium to the zinc in the paints changed with addition of zinc powder, which enhances the inhibition ability of the paint. For the red paint which 25 % zinc addition has the highest corrosion potential and the lowest corrosion current, thus, better corrosion resistance. The possible reasons for such behaviour may be addressed as follows. Firstly, zinc powder addition increase the formation of amorphous phase within the matrix of the paints thereby enhance the corrosion resistance property of the mild steel compared to samples with little or no zinc powder addition. This implies that samples coated with 25 % zinc addition have the highest corrosion resistance. Secondly, increasing in the volume fraction of the austenite phase within the matrix of the paint contribute to the improving inhibition ability, because austenite phase has better corrosion resistance than the ferrite phase [19], [20].

Certain condition needs to be met prior to self-passivation, as suggested by Yang, et al. [20] in formula (5).

$$E_{e,c} \geq I_{max} \quad (5)$$

where $E_{e,c}$ is the equilibrium potential of depolarizer in the cathodic reducing reaction and I_{max} is the current density of the depolarizer. From Table 5, it can be observed that Equation 5 has been satisfied. The corrosion potential and corrosion current of the samples are stable for the mild steel coated with 25% Zinc powder addition at ≈ -0.6505 V and $5.40 \cdot 10^{-8}$ A respectively.

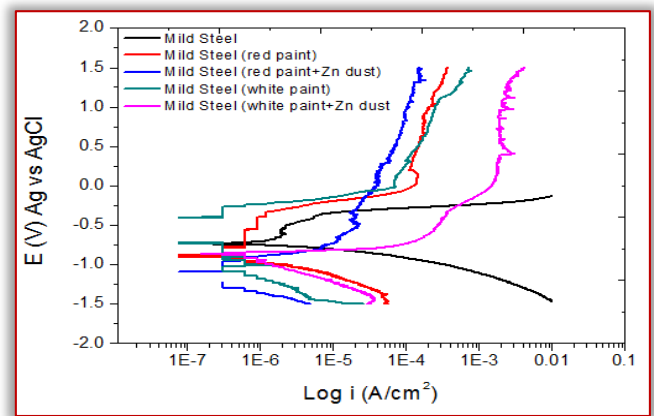


Figure 9: Potentiodynamic Anodic Polarization Plots of Mild Steel Immersed in Sea Water with and Without Zn Powder Addition

Table 5: Electrochemical corrosion parameters of mild steel immersed in sea water with and without Zn powder addition

Sample	Corrosion Current (I_{cor}) (10^{-8} A)	Corrosion Current Density	Corrosion Potential (E_{cor}) (10^{-8} V)
Mild steel	1.371E-06	2.17E-06	-0.738
Mild steel (white paint)	5.681E-07	9.47E-07	-0.406
Mild steel (red paint)	4.921E-07	7.81E-07	-0.501
Mild steel (red paint + 25 % zinc powder)	5.40E-08	9.00E-08	-0.6505
Mild steel (white paint + 25 % zinc powder)	5.40	1.60E-07	-0.6001

□ Surface Morphology

Figure 10 (a)-(d) show the surface morphology of some corroded samples. Presence of pit corrosion can be seen. The sizes of pits are more pronounced in Figure 10(b) compared to Figure 10(a) due to high inhibition efficiency of red paint. When zinc powder was added, there is a reduction in the amount of the pits visible in Figure 10 (c) and (d). The addition of zinc powder enhances the inhibition efficiency and significantly reduces the corrosion of the samples. It can be observed that samples without zinc addition are more badly corroded. The attack may be due to presence of salinity and chloride in the sea water. The reactions of these substance causes variation in layer thickness of the coating, which lead to localized corrosion characterized by depression or pit formation. Thus, there is a rapid inward penetration of oxygen at the exposed region for the formation iron oxide [14]. Pit formation may also be attributed to ionic migrations, which are influenced by the applied voltage [5]. With the addition of the zinc powder, the process is retarded due to better adhesion of the paints on the surface of the mild steel. Addition of zinc powder does not completely stop the corrosion process. Nevertheless, there is an improvement in reduction of corrosion rate when compared with other samples.

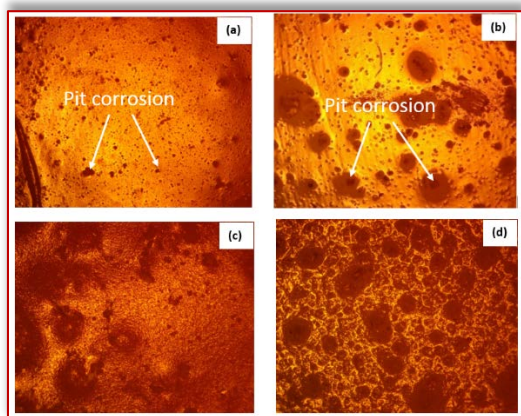


Figure 10: Surface morphology of the corroded samples (a) coated with red paint, (b) coated with white paint, (c) coated with white paint and 10 % zinc powder addition and (d) coated with white paint and 10 % zinc powder addition

CONCLUSIONS

This study has shown that:

- Addition of zinc powder to the locally procured Villa Gloss and Silka Lux Marine Enamel paints improved the corrosion resistance of the mild steel.
- The corrosion rate stabilised at approximately 0.10 mmpy when zinc powder added was above 15 %. This result was achieved independent of the exposure time.
- Zinc powder addition to both paints was beneficiary to the corrosion potential and corrosion current.
- Surface morphology of the samples revealed pit corrosion characteristics due to the inward penetration of oxygen at the exposed region.

Nomenclature

- A₁ uncoated sample.
 A₂ sample coated with 10 ml white paint + 0% zinc powder.
 A₃ sample coated with 10 ml red paint + 0% zinc powder.
 B₁ sample coated with 10 ml white paint + 5% zinc powder additive.
 B₂ sample coated with 10 ml red paint + 5% zinc powder additive.
 C₁ sample coated with 10 ml white paint + 10% zinc powder additive.
 C₂ sample coated with 10 ml red paint + 10% zinc powder additive.
 D₁ sample coated with 10 ml white paint + 15% zinc powder.
 D₂ sample coated with 10 ml red paint + 15% zinc powder additive.
 E₁ sample coated with 10 ml white paint + 20% zinc powder additive.
 E₂ sample coated with 10 ml red paint + 20% zinc powder additive.
 F₁ sample coated with 10 ml white paint + 25% zinc powder additive.
 F₂ sample coated with 10 ml red paint + 25% zinc powder additive
 C_r corrosion rate (mmpy)
 W weight loss (milligrams)
 A surface area of the sample (cm²)
 T time of exposure of the samples in hour(s)
 ρ metal density (g/cm³)
 L length of the sample (cm)
 B breadth of the sample (cm)
 T thickness of the sample (cm)

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